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Investigation of localized corrosion resistance of type 441 stainless steel annealed at different temperatures by means of a metastable pitting analysis

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The localized corrosion resistance properties of type 441 stainless steel used in the manufacturing of boiler heat exchangers were investigated by means of metastable pitting events analysis, observed in the cyclic potentiodynamic anodic curves. The experimentation was carried out on specimens obtained from not annealed and in-line annealed pipes at 700 and 900 °C. The Cyclic Potentiodynamic Polarization tests were conducted in neutral NaCl solutions characterized by chloride concentrations of 125 and 500 ppm. The results obtained from the analysis of the characteristic potentials and the metastable pitting events, determined from the experimental curves, showed that the localized corrosion resistance performances of type 441 stainless steel are higher after the annealing at 900 °C if compared to that at 700 °C.

KEYWORDS: FERRITIC STAINLESS STEEL, LOCALIZED CORROSION RESISTANCE, METASTABLE PITTING, ANNEALING TREATMENTS

INTRODUCTION

On condensing boiler heat exchangers, an effective alternative to AISI 304 and AISI 316 austenitic steels in terms of mechanical and corrosion resistance properties is type 441 ferritic stainless steel [1]. The absence of nickel makes type 441 cheaper and resistant to stress corrosion cracking in chlorides contaminated environments at temperatures higher than 50 - 60 °C [2]. The high content of chromium produces a stable and consistent passivation film, improving pitting corrosion resistance properties [3-5]. The heat exchangers are produced starting from the cold bending process of 441 stainless steel metal sheets into circular cross section pipes longitudinally welded. Afterwards, an annealing heat treatment is carried out to remove residual stress caused by previous plastic deformation and welding processes and to improve the pipe formability. The circular section pipes are at first calendered and bended to produce an elliptical-like section and then the coil shaped heat exchanger. Samples were obtained from untreated heat (UT) rectilinear pipes and annealing treated rectilinear pipes at temperatures of 700 °C (AT700)

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and 900 °C (AT900). The localized corrosion properties of type 441 stainless steel were evaluated in chloride environments by means of Cyclic Potentiodynamic Polarization (CPP) tests. Two chlorides concentrations of 125 ppm and 500 ppm were considered in this study. A routine in Visual Basic (VB) running in Excel was implemented to evaluate the characteristic potentials of the CPP curves and to determine the corrosion resistance properties in terms of localized corrosion behavior and metastable pitting.

Materials and methods

The chemical composition of type 441 stainless steel, shown in Tab. 1, is characteristic of a stabilized ferritic stainless steel with high resistance to stress corrosion cracking.

Tab.1 - Chemical composition (wt.%) of 441 stainless steel. / Composizione chimica (% in peso) dell'acciaio inossidabile tipo 441.

%C	%Si	%Mn	%P	%Cr	%Ti	%Nb
0.02	0.49	0.45	0.03	17.80	0.14	0.38

The specimens were obtained by cutting rectangular metal sheets from the rectilinear calendered tubes used in the heat exchanger before they undergo the bending process that turns them into a coil-shaped heat exchanger. The CPP tests were conducted to investigate type 441 stainless steel behavior concerning its localized corrosion properties in two neutral sodium chloride electrolytic solutions of 125 ppm and 500 ppm. CPP curves were recorded at room temperature by means of Gamry Reference 600 potentiostat and an electrochemical cell in the common three-electrodes configuration, using a saturated calomel electrode (SCE) as reference electrode, a titanium activated wire as counter-electrode and the examined stainless steel as working electrode. Before the electrochemical investigations, the 441 specimens were prepared starting from the electrical connection to a wire. Afterwards, the surfaces of the samples were cleaned with n-hexane and finally a polyimide tape was applied to insulate the specimens, leaving exposed to the environment a circular surface area of 1.13 cm^2. Once the specimen was immersed in the testing solution, the Open Circuit Potential (OCP) was monitored for approximately 15 to 30 minutes; when the OCP of the working electrode reached a steady state condition, the ohmic resistance of the solution was determined by means of Electrochemical Impedance Spectroscopy (EIS) with a frequency range of 100 kHz - 1 Hz, an amplitude of 10 mV and 10 points $decade^{-1}$. After the EIS was completed, the anodic CPP test started at -15 mV below the OCP, the scan rate was set to 0.166 mV s^{-1} and the current density threshold for reversing the polarization potential scan to 0.1 mA cm^{-2}. The reverse scan was stopped when the current density was lower than or in the range of the values of the current density associated with the passive region obtained in the forward potential scan. By means of a VB macro running in Excel, five parameters for each anodic CPP curve are determined: corrosion potential (E_{corr}), breakdown potential (E_{br}), protection potential (E_{prot}), metastable pitting potential (E_{mp}) and number of metastable events [6]. E_{br} is the potential associated with a rapid increase in current density at the end of the passive region while E_{prot} is the potential at the intersection point between the passive zone and the reverse scan part of the curve. A metastable pitting event was defined as a rapid increase in current density, with the corresponding growth rate, reaching a maximum and followed by a decrease up to values in the range of the passive zone. The VB routine identifies these events by considering only the maximum current density points with an associated growth rate, over a threshold value selected by the user from a range of values among all those determined in correspondence of each metastable pitting event during the forward scan of CPP curve. Finally, the routine returns a list of the metastable events. As a result, E_{mp} is the potential related to the first metastable pitting event.

RESULTS AND DISCUSSIONS

In Fig. 1 the characteristic potentials and regions of perfect passivity (blue area), imperfect passivity (green area) and metastable events (red outlined) obtained by the VB routine applied on the CPP curves are shown. The perfect passivity region delimited by E_{prot} and E_{corr} in 125 ppm Cl^- solution is wider for AT900 samples, while it is similar for UT and AT700 samples. For higher chlorides concentrations of 500 ppm Cl^- the perfect passivity regions of UT and AT900 samples are similar in extension, whereas the AT700 samples did not show perfect passivity area, indicating that the annealing treatment of 700 °C cannot guarantee the absence of localized corrosion risks of type 441 heat exchanger. Despite the high dispersion values in 125 ppm chloride solution, UT samples showed that the region of metastable events delimited by E_{mp} and E_{br} is wider than those of AT700 and AT900 samples in both the electrolytes, thus suggesting that the annealing treatment reduced the susceptibility to metastable pitting.

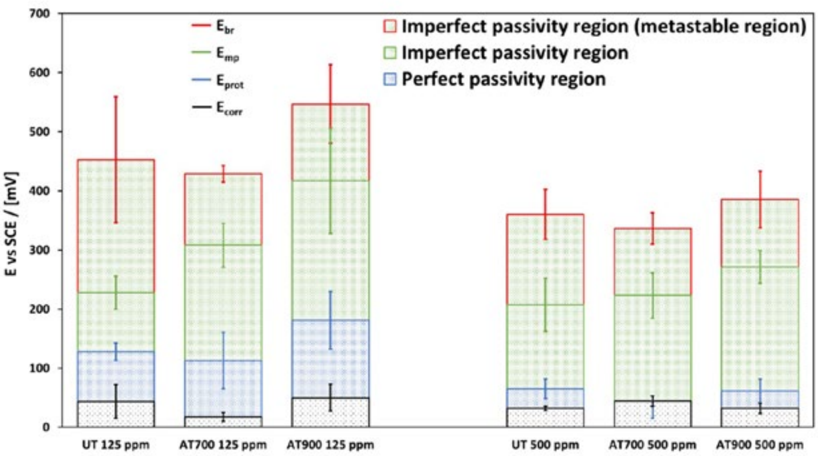

Fig.1 - Average values and standard deviations of characteristic potentials of UT, AT700 and AT 800 samples in the 125 and 500 ppm Cl^- solutions. The blue area corresponds to the perfect passivity region, the green area to the imperfect passivity region and the red outlined is the region in which metastable pitting events occur. / Valori medi e deviazioni standard dei potenziali caratteristici dei campioni UT, AT700 e AT900 nelle soluzioni di 125 e 500 ppm di Cl^-. L'area blu corrisponde alla zona di passività perfetta, l'area verde alla zona di passività imperfetta e la regione contornata di rosso è la zona in cui si verificano gli eventi di pitting metastabile.

Besides pitting corrosion, crevice corrosion was occasionally reported in correspondence of the perimeter of the exposed surface of each specimen; its occurrence determined the rejection of CPP curves corresponding to the 441 samples in which it was found. This rule was applied to all curves except for those corresponding to AT700 samples, for which crevice corrosion could not be avoided since it occurred in all the tests. Considering this experimental evidence, the potential for which the localized corrosion happened was called breakdown potential (E_{br}) and not pitting potential.

The increasing chlorides concentration effect is shown in Fig. 2, in which E_{br}, E_{prot} and E_{mp} average values and the standard deviations are displayed. The samples AT700 have the lowest values of E_{br} and E_{prot} in both the electrolytes, if compared to UT and AT900 specimens. The decreased localized corrosion resistance properties of AT700 could be attributed to the presence of precipitated intermetallic phases, such as Ti and Nb carbonitrides and Laves phases (e.g., Fe_2Nb) which occur mostly in the range of annealing temperatures of 600-850 °C for ferritic stainless steels, as suggested by literature observations [7-11]. Nevertheless, the E_{mp} values shown in Fig. 2c indicate that the increase in the annealing temperature significantly reduces the susceptibility to metastable pitting in 125 ppm Cl^- solution, as previously observed for the narrower metastable region (red outlined) of both the annealed specimens compared to UT in Fig. 1.

In 500 ppm Cl^- solution, the average values of the characteristic potentials are higher for AT 900 samples compared to those of the other samples, even if there is a significant overlap of standard deviations, in particular in the case of E_{br} and E_{prot} potentials (Fig. 2a and 2b, respectively). However, E_{mp} (Fig. 2c) is higher for AT900 samples taking into account the standard deviations, as already observed in the case of less concentrated solution.

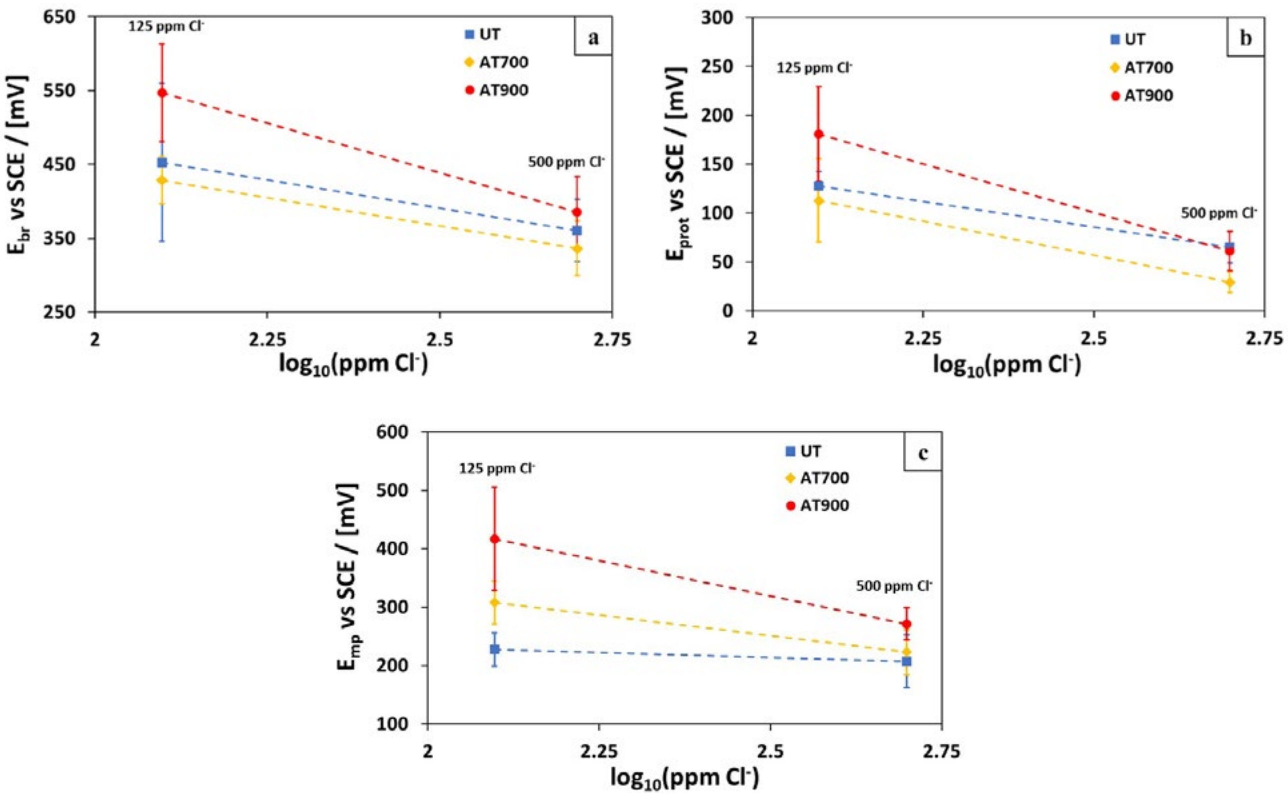

Fig.2 - Trends of the characteristic potentials of UT, AT700 and AT 900 samples as a function of the logarithm of chlorides concentration, corresponding to 125 and 500 ppm: a) E_{br}; b) E_{prot}; c) E_{mp}. / Andamento dei potenziali caratteristici dei campioni UT, AT700 e AT900 in funzione del logaritmo della concentrazione di cloruri, corrispondenti a 125 e 500 ppm: a) E_{br}; b) E_{prot}; c) E_{mp}.

The VB routine allowed to evaluate the average number and the corresponding standard deviations of metastable pitting events obtained by the analysis of the CPP curves (Fig. 3), thus confirming that increasing the annealing temperature of the heat treatment reduced the probability of metastable pitting nucleation in accordance with the observations of narrower metastable regions (Fig. 1) and higher values of E_{mp} (Fig. 2c) for AT700 and AT900 samples. This observation clearly applies for both chloride solutions, considering the standard deviations.

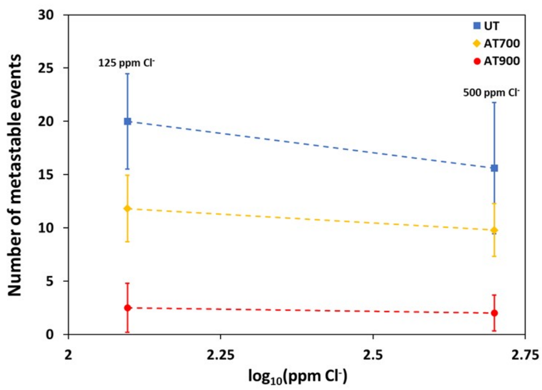

Fig.3 - Average numbers and standard deviations of metastable pitting events as a function of the logarithm of chloride concentrations. / Valori medi e deviazione standard del numero di eventi di pitting metastabile in funzione del logaritmo della concentrazione di cloruri.

In conclusion, this investigation showed that the assessment of metastable pitting events and the determination of the E_{mp} potential are both relevant tools for studying the susceptibility to localized corrosion of a stainless steel concerning the heat-treatment process and the aggressiveness of the environment. Moreover, considering that in some cases E_{br} cannot be related to pitting corrosion, such as for the AT700 samples in which crevice corrosion was unavoidable, the method proposed in this study could be reliable in such circumstances. Therefore, comparing E_{br} of different samples in contact with different corrosion environments could be of limited application for studying the susceptibility of a given stainless steel to localized corrosion.

CONCLUSIONS

In this study the localized corrosion resistance properties and metastable pitting susceptibility of 441 type stainless steel has been investigated by means of Cyclic Potentiodynamic Polarization curves evaluated by a Visual Basic routine running in Excel. The main results can be summarized as follows:

- the annealing treatment on ferritic 441 at 700 °C significantly reduced the localized corrosion resistance as a function of the aggressiveness of the environment, in particular in the 500 ppm Cl^- solution. This behavior can be most likely attributed to the formation of intermetallic phases (e.g., Nb and Ti carbonitrides, Fe_2Nb) enhanced by this specific annealing temperature. For higher annealing temperatures of 900 °C, those detrimental phases are most likely absent and the corrosion behavior is improved if compared to both the untreated and the 700 °C annealed ferritic stainless steel;
- the occurrence in nucleation of the metastable pitting events and the reduction of metastable pitting potential is reduced by the increment in the heat treatment temperatures, suggesting a lower risk of localized corrosion development;
- finally, the counting of metastable pitting events and the determination of metastable pitting potential can be considered both fundamental tools for studying the susceptibility to localized corrosion of the examined stainless steel, taking into account that the breakdown of passivity film cannot be always associated to the same type of corrosion (pitting vs crevice).

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Indagine sulla corrosione localizzata dell'acciaio inossidabile tipo 441 ricotto a differenti temperature attraverso un'analisi del pitting metastabile

In questo lavoro sono state indagate le proprietà di resistenza a corrosione localizzata dell'acciaio inossidabile tipo 441 utilizzato per la fabbricazione di scambiatori di calore per caldaie mediante l'analisi degli eventi di pitting metastabile osservati nelle curve anodiche potenziodinamiche cicliche. Lo studio è stato compiuto su provini ottenuti da tubi non ricotti e ricotti a 700 e 900 °C. I test di polarizzazione potenziodinamica ciclica sono stati condotti in soluzioni neutre di NaCl caratterizzate da concentrazioni di cloruri di 125 e 500 ppm. I risultati ottenuti dall'analisi dei potenziali caratteristici e degli eventi di pitting metastabile, determinati dalle curve sperimentali, hanno mostrato che le caratteristiche di resistenza a corrosione localizzata dell'acciaio inossidabile tipo 441 sono superiori dopo la ricottura a 900°C se confrontata con quella a 700°C.

PAROLE CHIAVE: ACCIAIO INOSSIDABILE FERRITICO, RESISTENZA A CORROSIONE LOCALIZZATA, PITTING METASTABILE, TRATTAMENTI DI RICOTTURA

TORNA ALL'INDICE >